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SPECIFICATION

1. Title of the Invention

Photochromic materials

2. Scope of the Patent Claims

(1) Photochromic material which contains a clathrate compound comprising host molecules and guest molecules of a photochromic substance.

(2) A photochromic material, according to claim 1, wherein the aforementioned host molecules are cyclodextrin molecules.

(3) A photochromic material, according to claim 1, wherein the aforementioned photochromic substance is spiropyran, a dithizone metal complex, a triphenylmethane-based dye or a fulgide.

3. Detailed description of the Invention

Industrial Field of Application

The invention concerns photochromic materials, and especially organic photochromic materials.

Prior Art

Photochromic compounds have been widely researched in the past, and even if just the organic compounds are considered then spiropyran, leuco-triphenylmethane dyes, imidazole indigo, thioindigo, dinitrobenzyl, pyridine, fulgide, stilbene, heterocyclic compounds and condensed multi-ring aromatic compounds, for example, have been investigated.

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Much research with spiropyran in particular has taken place in solution and in resins, and application of these systems has been attempted. With the condensed multi-ring aromatic compounds as well, dispersed systems in epoxy resins, poly(vinyl chloride), poly(methyl methacrylate) and polycarbonate have been researched and developed (Japanese Unexamined Patent Applications (Kokai) 49-114433 and 55-151518).

Problems to be Resolved by the Invention

However, these conventional photochromic materials present a difficulty with durability, and as yet no photochromic material which has good enough durability for practical use has been reported.

The aim of the present invention is to provide photochromic materials which have good durability, and this aim has been realized by means of the invention.

Means of Resolving These Problems

That is to say, the invention is a photochromic material which contains a clathrate compound comprising host molecules and guest molecules of a photochromic substance.

The host molecules in the clathrate compound which is used in the invention must be of a size which is suitable to take in (which is to say to enclose) one of the photochromic substance guest molecules. Cyclodextrin is preferred for the host molecules, and there are three types of cyclodextrin, namely α -, β - and γ -cyclodextrin, corresponding to the number (6, 7 or 8) glucose rings from which they are constructed. The

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internal diameters of the cavities in these materials are 6 Å, from 7 to 8 Å, and from 9 to 10 Å, respectively. One molecule of the photochromic substance which provides the guest molecules must be of a size which is suitable for enclosure in the corresponding cyclodextrin. Spiropyran, a dithizone metal complex, a triphenylmethane-based dye or fulgide, for example, can be used as the photochromic substance which provides the guest molecules.

The clathrate compounds in this invention are normally solids. The clathrate compounds preferably have the same numbers of host molecules and guest molecules, but the prescribed appearance and disappearance of color can be obtained provided that there is at least 10% of photochromic substance with respect to the number of host molecules.

To prepare a clathrate compound in this invention the photochromic substance is added to, and mixed with, an aqueous solution of cyclodextrin at room temperature and then it is pulverized immediately and stirred thoroughly. Subsequently, the photochromic substance/cyclodextrin clathrate compound is precipitated out and so it is recovered by filtration, washed and dried under reduced pressure. The target clathrate compound can be obtained as a powder in this way.

The photochromic materials of this invention preferably include a medium for dispersing the clathrate compound in a molecular form. If a liquid such as xylene or toluene is used as the medium for the

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clathrate compound then the photochromic material is a solution, and if an organic polymer such as poly(methyl methacrylate) or polystyrene is used then the photochromic material is a solid. The clathrate compound is preferably included in an amount of from 0.0001 wt% to 15 wt% with respect to the medium so that the photochromic material forms or loses its color depending on whether or not it is being irradiated with light (for example sunlight).

Action and Effect of the Invention

Photochromic materials which did not exist in the past in which a photochromic substance is enclosed in host molecules can be obtained by means of this invention. In comparison with the conventional systems where the photochromic substance is dispersed directly in a molecular form in a medium without using host molecules, the durability of the photochromic material is improved in the case of the invention where a clathrate compound in which the photochromic substance is enclosed in host molecules is dispersed in a molecular form, and the color of the photochromic material when it is not being irradiated with light is lightened. The reason for the improvement in durability is not clear, but it is thought that the deterioration in durability is due in the main to interactions between the photochromic substance and the medium, and in this invention the direct interaction of the medium and the photochromic substance is prevented by the host substance of the clathrate compound and it

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is conjectured that the durability is improved as a result of this.

The invention is described in more detail below by means of illustrative examples but, of course, the scope of the invention is not limited by these examples.

Illustrative Examples

Example 1

Water (10 g) was added to 10 g of γ -cyclodextrin (manufactured by Tokyo Kasei) and stirred to form a slurry. Next 0.1 g of 1,3,3-trimethylindolino-6'-nitro-8'-methoxybenzopyrylsipran (Compound (I)) which had been prepared using a known method was added and mixed at room temperature and then pulverized directly and thoroughly mixed. The precipitated clathrate compound was recovered by filtration and washed with xylene and then the product was dried under reduced pressure and a clathrate compound which has approximately equal numbers of guest molecules of compound (I) and host molecules of γ -cyclodextrin was obtained. A solution (6×10^{-5} mol/l) of this clathrate compound dissolved in an amount of 0.01 g in 1000 ml of xylene and a xylene solution of the same concentration (6×10^{-6} mol/l) of compound (I) were introduced into Pyrex containers of liquid depth 20 mm. Under fluorescent light the former was a lighter yellow than the latter, and they both assumed a blue coloration of a similar intensity on irradiation with sunlight. On visual observation, the latter lost its blue coloration

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in sunlight after about 1 hour 15 minutes but the former was blue for about 5 hours. The durability had been improved by a factor of about four times by forming the clathrate compound.

Example 2

An experiment was carried out in the same way as in Example 1 using β -cyclodextrin (manufactured by Tokyo Kasei). On forming the clathrate compound the material was light yellow under fluorescent lighting and the durability was improved by a factor of about three times.

Example 3

An experiment was carried out in the same way as in Example 1 using β -cyclodextrin and 4-amino-2,6-dichlorophenylmercury dithizonate (compound(II)). On forming the clathrate compound the material was light colored under fluorescent lighting and the durability was improved by a factor of about three times.

Example 4

An experiment was carried out in the same way as in Example 1 using γ -cyclodextrin and compound(II). On forming the clathrate compound the material was light colored under fluorescent lighting and the durability was improved by a factor of about two times.

Example 5

An experiment was carried out in the same way as in Example 1 using α -cyclodextrin and 4-aminophenylmercury dithizonate (compound(II)). On forming the clathrate compound the material was light

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colored under fluorescent lighting and the durability
was improved by a factor of about three times.

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